

# UNITED STATES ENVIRONMENTAL PROTECTION AGENCY REGION 10 HANFORD PROJECT OFFICE

712 Swift Boulevard, Suite 5 Richland, Washington 99352

July 16, 2004

Steve Zappe State of New Mexico NMED Hazardous Waste Bureau 2905 Rodeo Park Drive East, Bldg 1 Santa Fe, New Mexico 87505

Subject: Hanford Site K Basins Sludge, Classification Documents

Dear Mr. Zappe:

I appreciate the opportunity to talk with your earlier this week regarding sludge from the Hanford Site's K Basins, and the plans to treat and send this transuranic waste to the Waste Isolation Pilot Plant for disposal. Although it was clear that you have a good understanding of the origin, characteristics, and classification of the sludge, I promised to send you several key documents regarding sludge classification to ensure they are in your records. Enclosed are three key letters that document actions by the U.S. Department of Energy, the State of Washington, and the U.S. Environmental Protection Agency that document the determination that the sludge is transuranic waste and is not Resource Conservation and Recovery Act (RCRA) toxic waste. You are welcome to give me a call at 509-376-9884 in the future regarding any aspects of the Hanford K Basins sludge project.

Sincerely,

Xarry Saclois
Larry Gadbois

EPA's Hanford Site K Basins Project Manager

Cc: Hanford Administrative Record, 100-KR-2

(On-line at www2.hanford.gov/arpir/search/simple\_search.cfm)

Enclosures:

1) Letter from P.G. Loscoe, DOE dated 2 December 1999, "K Basins Sludge Classification". This letter documents classification of the sludge by DOE as TRU waste.

2) Letter from P.G. Loscoe, DOE dated 8 August 2000, "Transmittal of Final Laboratory Data Reports for Toxicity Characteristic Leaching Procedure (TCLP) Analysis Performed on K-East (KE) Basin Sludge Samples".

This letter presents DOE's determination that Hanford K Basin sludge does not designate as toxic per RCRA.

3) Letter from Joan K. Bartz, State of Washington, and Larry Gadbois, EPA dated 14 September 2000, "Response to Transmittal of Final Laboratory Data Reports for Toxicity Characteristic Leaching Procedure (TCLP) Analysis Performed on K-East (KE) Basin Sludge Samples"

This letter documents concurrence by the State of Washington and EPA Hanford K Basin sludge does not designate as toxic per RCRA.

040740



# Department of Energy

9958990 CC RECD: 12/08/99

Richland Operations Office P.O. Box 550 Richland, Washington 99352

00-SFO-043

DEC 0 2 1999

Mr. R. D. Hanson, President Fluor Daniel Hanford, Inc. Richland, Washington 99352

Dear Mr. Hanson:

# CONTRACT NO. DE-AC06-96RL13200 - K BASINS SLUDGE CLASSIFICATION

The U.S. Department of Energy, Richland Operations Office (RL) letter to R. D. Hanson, Fluor Daniel Hanford, Inc., from P. G. Loscoe, "Spent Nuclear Fuel (SNF) Sludge Treatment Management Evaluation Recommendation," 99-SFD-143, dated July 6, 1999, provided formal acceptance of the contractor proposal for interim storage of K Basins sludge prior to treatment and disposal to be coordinated with other Remote-Handled Transuranic (RH-TRU) waste on site. One of the assumptions made in the proposal was that upon removal, the K Basins sludge becomes a waste that would designate as TRU waste.

RL has formalized the classification of the K Basins sludge after removal. The Offices of Chief Counsel for RL and Waste Isolation Pilot Plant (WIPP) concur with this classification. The enclosed memorandum from WIPP states that the sludge could be classified as RH-TRU waste. Closure of this issue helps to eliminate the risks associated with the current sludge management path forward.

The K Basins sludge is a TRU waste. Presently, the sludge is so commingled with SNF in the basin, that it cannot be managed separately. Once the SNF and the retrievable debris are separated out, the remaining sludge will be removed. Upon removal from the basins, the sludge will classify as RH-TRU waste and be dispositioned.

If you have any questions, please contact me, or you may contact Robert G. Holt of my staff on (509) 376-1062.

Sincerely,

P. G. Loscoe, Director

Office of Spent Nuclear Fuels

SFO:RGH

Enclosure

cc w/encl:

L. M. Johnson, CHI

J. D. Ludowise, CHI

J. W. Foster, DESH

R. P. Ruth, DESH

J. A. Swenson, DESH

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E. W. Gerber, FDH

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R. G. Jones, FDH

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R. M. Suyama, FDH

D. B. Van Leuven, FDH

R. B. Willard, FDH

T. Choho, NHC

C. A. Petersen, NHC

W. W. Rutherford, NHC

Memorandum

Date: October 26, 1999 To: Barbara Williamson Clc: Elizabeth Rose From: Barry Goldstein Subject: K-Basin Sludges

One of the sources of confusion on the issue of whether K-Basin sludges are RH-TRU wastes stems from the fact that the radioactive wastes in the sludges are derived from SNF. There is little guidance as to how to classify a radioactive waste type derived from a radioactive waste type. For example, a pump used to move HLW liquids from one location to another is now contaminated with HLW, and is declared as waste. Is the pump now HLW? According to statutory and regulatory definitions, HLW results from the reprocessing of SNF. The pump did not result from such reprocessing, so what type of radioactive waste is it?

DOF Order 5820.2A answered the question for radioactive wastes derived from TRU wastes in that the definition of TRU waste explicitly stated that "regardless of source or form", waste that met the radiological criteria of TRU waste was TRU waste. I know of no equivalent guidance for SNF. Does radioactive waste derived from SNF remain SNF, or does one look to the sludges themselves without regard to source or form?

Clearly, the radioactive wastes in the K-Busin sludges are derived from SNF, and not from coment, dust, biological debris, etc. Unfortunately, the new DOE Order 435.1 no longer allows one to disregard form or source. This is the crux of the problem.

Regardless, I agree, based on the corrected guidance you sent me, that certain radioactive wastes derived from SNF can be managed as RH-TRU. These would include pieces and corrosion products of the SNP found in the K-Basin sludges. It would thus appear that the radioactive wastes in the K-basin sludges are RII-TRU. As such, it is appropriate to label the K-Basin sludges as RII-TRU. However, I reach that result from a different analysis using the corrected guidance and decision tree. The answer to the first question of the decision tree is "Yes" for the SNF particulates and corrosion products in the sludges. Then we go the question "Is it fuel withdrawn from a nuclear reactor after irradiation?". The answer is again yes for the SNF particulates and corrosion products in the sludges. Obviously, the constituent elements of the SNF have NOT been separated by reprocessing; they are the result of unintentional chemical reactions. The question then becomes "Is it test specimens, . . ". The corrected guidance tells us that "fuel pin fragments and diverse particulate that cannot be readily retrieved and packaged with the fuel assemblies and intact pin" may be managed as RII-TRU. The radioactive wastes in the sludges satisfy this description. Hence, I agree that the sludges are contaminated with RH-TRU waste, and, as such, must be managed as RH-TRU waste for purposes of disposal (assuming their surface dose rate exceeds 200 nirem/hr.).

I will recommend that WIPP revise the decision tree to reflect the corrected guidance.



# **Department of Energy**

Richland Operations Office P.O. Box 550 Richland, Washington 99352 HANFORD PROJECT OFFICE

AUG 8 2000

ENVIRONMENTAL PROJECTION
AGENCY

00-SFO-135

AUG 0 8 2000

Ms. Joan K. Bartz Department of Ecology 1315 West Fourth Avenue Kennewick, Washington 99336

Mr. Larry E.Gadbois U.S. Environmental Protection Agency 712 Swift Blvd. Suite Five Richland, Washington 99352

#### Addressees: -

TRANSMITTAL OF FINAL LABORATORY DATA REPORTS FOR TOXICITY CHARACTERISTIC LEACHING PROCEDURE (TCLP) ANALYSES PERFORMED ON K-EAST (KE) BASIN SLUDGE SAMPLES

References: (1) Winters, W. I., August 2000, "Narrative Report for TCLP Testing and Analyses on K-East Basin Floor and Pit Composite Sludge," HNF-1704, Rev. 0. 222-S Laboratory Fluor-Hanford, Inc., Richland, Washington (Attachment 1).

- (2) Silvers, K. L., Wagner, J. J. and Steele, R. T., August 2000, "TCLP Preparation and Analysis of K-East Basin Composite Sludge Samples," PNNL-13280, Pacific Northwest National Laboratory, Richland, Washington (Attachment 2).
- (3) Makenas, B. J., April 2000, "Data Quality Objectives for Analysis of Hanford K Basin Sludge to Support Transport to and Storage in T Plant," HNF-5345, Rev. 0.
- (4) Baker, R. B. et al., July 2000, "Sampling Analysis Plan for Sludge from the 105-K Basins to Support Transport to and Storage in T Plant," HNF-6974 Rev. 0.

The final data packages for the TCLP and total metals analysis on the K Basins sludge samples have recently been completed, including quality assurance reviews, and are attached for your review References (1) and (2). These data are consistent with the preliminary information that was shared with both of you during a meeting held on June 28, 2000.

The Spent Nuclear Fuel (SNF) Project has presumed for the past two years that the sludge in the K Basins would be designated as dangerous waste for heavy metals. This was noted as a conservative assumption, as the TCLP analyses had not yet been completed.

The SNF Project and my staff began meeting with you on this topic in November 1999, to involve you in our plans for conducting the TCLP analyses on the KE Basin sludge. At that time, and during subsequent meetings, we discussed and agreed on the approach to be used. The agreements reached in these meetings allowed us to proceed with the TCLP analyses with a good understanding of how the data would be interpreted and used by our project and by the State of Washington Department of Ecology (Ecology). The specific agreements made during those meetings included the following:

- 1. The method in which sludge samples had been collected from the basin, including composites was sufficient to ensure representative samples were available for analyses.
- 2. The sample size for TCLP, although smaller than typically analyzed in a non-radioactive environment, was sufficient given the methodology for running duplicates and splits.
- 3. TCLP analysis for organic constituents was not necessary, based on process knowledge of the waste. Only the heavy metals of concern would be analyzed.
- 4. Both the KE and K-West (KW) Basins contain SNF from N Basins. The accumulated sludge in the KE and KW Basins would be considered sufficiently similar that TCLP data from the KE Basin could be used to calculate the TCLP concentration in the KW Basin by direct comparison to the total metals data in each basin. This would eliminate the need to run separate TCLP analyses of the sludge from the KW Basin.
- 5. Holding times for the KE Basin samples could exceed the standard times for TCLP analysis, since only metals were being analyzed and metals would not be affected by longer holding times.
- 6. We were to provide the revised Data Quality Objective document Reference (3) and the Sampling and Analysis Plan Reference (4) to you for review and comments. These were provided and your comments were satisfactorily addressed prior to issuance of both documents.

The TCLP data for the KE Basin sludge indicate the heavy metal concentrations are far below the threshold for regulation as dangerous waste and that these data are suitable for use in waste designation. Upon your review of the attached data packages, we would appreciate your concurrence to our conclusion. We will prepare a formal waste designation letter to you in the near future that will address both the heavy metals and the characteristics of ignitability and reactivity.

We look forward to your reply and concurrence, as requested above, by August 22, 2000. If you have questions, please contact me, or you may contact Oscar M. Holgado of my staff on (509) 373-0589.

Sincerely,

P. G. Loscoe, Director

Office of Spent Nuclear Fuels

### SFO:OMH

#### Attachments

cc w/attachs:

J. H. Wicks, DESH

M. D. Ellefson, FHI

R. M. Suyama, FHI

W. W. Rutherford, FHI

D. B. Van Leuven, FHI

D. J. Watson, FHI

# CORRESPONDENCE DISTRIBUTION COVERSHEET

Author J. H. Wicks, FH P. T. Day, 376-4827 Addressee
P. G. Loscoe
RL

Correspondence No. FH-0100738 February 7, 2001

Subject:

CONTRACT NUMBER DE-AC06-96RL13200 – COMPLETION OF WASTE DESIGNATION FOR K BASIN SLUDGE WASTE STREAMS

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Attachment FH-0100738

Designation of K Basins Sludge Waste Streams

Consists of 13 pages including cover page

# CORRESPONDENCE DISTRIBUTION COVERSHEET

Author

J. H. Wicks, FH P. T. Day, 376-4827 Addressee

P. G. Loscoe

Correspondence No. FH-0100738 February 7, 2001

RL

CONTRACT NUMBER DE-AC06-96RL13200 - COMPLETION OF WASTE

Subject:

DESIGNATION FOR K BASIN SLUDGE WASTE STREAMS

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# **Designation of K Basins Sludge Waste Streams**

January, 2001

# Background

### **Purpose**

The Spent Nuclear Fuel Project will remove spent fuel and residual sludge material from the 105-KE and 105-KW Basins over the next several years. An estimated fifty cubic meters of sludge is anticipated from the floor and pits of the basins, from the fuel canisters, and from washing of fuel. Upon removal from the KE and KW Basins, the sludge will classify as a remote-handled transuranic waste (Loscoe, 1999). The sludge waste streams will be packaged and transferred to the T Plant complex in the 200-W area for interim storage until the waste can be prepared for shipment to the Waste Isolation Pilot Plant or other approved location.

This document presents the Hanford Site waste designation for the sludge waste streams in accordance with WAC 173-303-070. Process knowledge and test data from sampling and analysis of sludge and spent nuclear fuel are presented to support the designation.

### Description of Waste Streams and Generating Process

The KE and KW Basins were constructed in the 1950s to store spent nuclear fuel from Hanford reactors. Fuel storage has been the sole function of the basins from initial operations to the present. The basin water has been conditioned by pH adjustment, temperature control, filtration of particulate material and removal of radionuclides using ion exchange resins.

Spent nuclear fuel in the KE Basin is stored in open top canisters, some of which have screened bottoms. The fuel in these open top canisters has corroded to varying degrees. These fuel corrosion products, along with environmental particulates (e.g. windblown dust, vegetation fragments) and corrosion products from fuel racks and other facility components have combined to create a considerable amount of residual sludge material in the KE Basin. This sludge currently resides on the floor of the basins, in the basin pits, and within the fuel storage canisters.

Fuel in the KW Basin has been stored in closed stainless steel and aluminum canisters, which have released far fewer corrosion products to the basins. The KW Basin has some sludge accumulations on the floor, in pits and within fuel canisters, but the total sludge quantity and the radioactive material present are in much smaller quantities.

During deactivation of the basins, two primary waste streams will be generated:

- Canister and fuel wash shadge. When the fuel is removed and cleaned in preparation for dry storage, the residual sludge in the fuel canisters will be removed and the fuel will be washed to remove adhered corrosion products. The material removed from the fuel will be screened and particulate larger than 0.25 inch will be dried and managed as spent fuel. Very small particulate material will disperse in the water and be collected in the water treatment system. The remaining sludge (i.e., particles less than 0.25 inches but sufficiently large and dense to settle) is referred to as canister and fuel wash sludge. This sludge will be highly radioactive and have relatively high concentrations of uranium, uranium oxides, and related fuel corrosion products. As packaged for storage, the canister and fuel wash sludge will contain 30% 40% water by weight. The nominal volume estimate for canister and fuel wash sludge is 3 cubic meters.
- Floor and pit sludge. Floor and pit sludge will consist of the sludge currently residing on the floor and in several pits used to accumulate sludge in the basins, along with any additional sludge released from fuel canisters during fuel retrieval operations. The floor and pit sludge composition includes more environmental particulate and nonradioactive corrosion products (e.g., iron oxides), and

contains proportionally less fuel corrosion products. As packaged for storage, the floor and pit sludge will contain 30% - 40% water by weight. The nominal volume estimate for floor and pit sludge is 47 cubic meters.

The canister and fuel wash sludge will be packaged in vented, stainless steel canisters and stored underwater in T Plant's fuel pool. The floor and pit sludge will be packaged in similar vented, stainless steel canisters, but will be stored in empty process cells at T Plant rather than underwater.

## Summary of Sampling and Laboratory Test Data

The sludge streams each contain a significant quantity of radioactive material resulting from corrosion of spent nuclear fuel, including uranium, plutonium and fission products. To maintain personnel exposure to these radioactive materials as low as reasonably achievable (ALARA), the Spent Nuclear Fuel Project has followed the principles set forth in the *Joint EPA NRC Guidance on Testing Requirements for Mixed Radioactive and Hazardous Waste* (62FR 62079 - 62094). Specifically, knowledge of the sludge properties and the generating process has been used to limit the amount of sampling and laboratory testing, when such knowledge is adequate to designate the waste. Additionally, sampling and laboratory testing have sometimes been performed with smaller samples than would typically be obtained in order to maintain personnel exposure as low as reasonably achievable.

There have been three primary sludge sampling campaigns: floor and pit sludge from KE Basin: KE Basin canister sludge; and KW Basin canister sludge. Additionally, analyses have been performed on corroded and uncorroded spent nuclear fuel. The fuel analyses were performed specifically to support fuel removal and drying operations; however, the data are helpful in evaluating the ignitability and reactivity of the canister and fuel wash sludge

Table 1 summarizes the types of laboratory test data available for the sludge streams. When relevant for designation, more detailed descriptions of the samples obtained and test results are provided later in this document.

Table I - Test Data Related to KE and KW Sludge Waste Streams Designation

Waste Stream	105-KE Basin	105-KW Basin
Floor and pit	Total metals	No data
sludge	TCLP metals	
	PCBs	
	Volatile organic analytes	
	Semi-volatile organic analytes	
	pΗ	
	Anions	
	X-ray diffraction	•
•	X-ray fluorescence	
	Total organic carbon	
	Reactivity screening (RSST)	
Canister	Total metals	Total metals
sludge	TCLP metals	PCBs
	PCBs	pH
	рH	Antons
	Anions	X-ray diffraction
•	X-ray diffraction	Total organic carbon
	Total organic carbon	
	Reactivity screening (RSST)	
Fuel and fuel	No data	Thermogravimetric analysis
pieces		Ignition testing

Note that floor and pit sludge has not been sampled from the KW Basin. Because KW Basin fuel is better contained, and other operating conditions have been similar to those in the KE Basin, the KE sludge is believed to be representative of KW sludge. With respect to TCLP testing, Ecology and EPA were involved in development of Data Quality Objectives (Makenas, 2000) and a Sampling and Analysis Plan (Baker, Welsh and Makenas, 2000) and agreed that test data from KE sludge samples could be used, in combination with KW sludge total metals data, to designate KW sludge (Bartz and Gadbois, 2000). This rationale can be reasonably inferred to most other parameters of interest in designation of sludge.

## Regulation Under Other Laws

The K Basins studge waste streams will contain both a solid waste component and a radioactive component subject to regulation under the Atomic Energy Act. The radioactive component of the studge waste stream consists largely of uranium, plutonium, americium, and fission products from the spent nuclear fuel stored in the basins. With respect to designation under the Resource Conservation and Recovery Act Hazardous Waste Regulations (40 CFR 260 through 268) and the Washington State Dangerous Waste Regulations (WAC 173-303), only the solid waste component of the sludge is subject to regulation. The radioactive component of the waste is excluded from regulation as source material in accordance with 40 CFR 261.4(a)(4). Under the DOE classification system for radioactive waste, the K Basins sludge has been designated remote-handled transuranic waste upon removal from the basins (Loscoe, 1999).

Polychlormated biphenyls have been identified in samples of KE floor and pit sludge in concentrations that exceed 50 ppm, but less than 500 ppm. PCBs have been detected in canister sludge from KE and KW in concentrations well below 50 ppm. The source of these PCBs is not known. Due to the as-found PCB concentration in the floor and pit sludge, the storage and disposal of K Basins sludge streams will be regulated as PCB remediation waste under the Toxic Substance Control Act PCB regulations of 40 CFR 761.61.

# Designation

Based on knowledge of the materials and processes that generated the sludge, along with test data, the sludge waste streams are not regulated under WAC 173-303. The following sections describe in detail the rationale and data leading to this designation.

## Listed Waste Designation

The sludge waste streams are not designated as F. K. U or P listed dangerous waste. Listed waste numbers can be only be assigned based on knowledge of certain materials and/or processes, none of which have occurred in the KE and KW Basins. The KE and KW Basins were used solely for fuel storage. The sludge is not a U or P listed discarded chemical product, nor are any of the K listed specific or F listed non-specific dangerous waste sources applicable to this waste stream. Additionally, there have been no known discharges or spills of listed waste to either basin.

## Characteristic Waste Designation

## Ignitability (D001)

The two sludge waste streams are not designated as ignitable (D001). The liquid portion of the sludge waste stream is water, and thus does not exhibit a flash point. The sludge contains no strong exidizers. Regarding the non-liquid portion of the sludge, the sludge contains radioactive corrosion products from spent nuclear fuel, which could include some uranium metal fragments and uranium hydride. Under certain conditions, uranium metal and uranium hydride can ignite. Additionally, some potentially ignitable zirconium from the fuel cladding could be present in the sludge. While the radioactive component of the sludge is not strictly subject to regulation under WAC 173-303, the sludge as a whole has been evaluated against WAC 173-303-090(5)(a)(ii) and determined not to meet the definition of ignitability for non-liquids. This definition reads as follows

It is not a liquid and is capable, under standard temperature and pressure, of causing fire through friction, absorption of moisture or spontaneous chemical changes and, when ignited, burns so vigorously and persistently that it creates a hazard.

The regulations do not specify quantitative test methods or numerical limits for determining whether a non-liquid would be ignitable. Designation of the sludge streams as non-ignitable is based on knowledge of the sludge composition, observed properties of sludge in the basins, observed properties of sludge and fuel in the laboratory, and laboratory test data. This information is summarized below.

• The concentration of uranium metal, uranium hydride and zirconium in the sludge streams will be low. The fuel corrosion products are largely oxidized uranium, with much smaller amounts of zirconium oxides from the zircaloy fuel cladding. The metal and hydride in sludge are only transient components of the corrosion products, which are readily oxidized in the basins and under the anticipated storage conditions for the sludge. The uranium metal concentration in the KE floor and pit sludge is estimated to be less than 0.2% (as settled sludge), with no uranium hydride or unoxidized zirconium (Pearce, 2000). Since fuel in the KW Basins is stored in closed canisters, uranium metal, uranium hydride and zirconium have not been released to the KW floor and pit sludge in significant concentrations.

Canister and fuel wash sludge is expected to contain higher concentrations of uranium metal, and possibly some hydride. Test data indicate that canister sludge contains less than 2% uranium metal (Pearce, 2000). Estimate of the uranium hydride concentration in canister sludge is also less than 2%. The amount of zirconium present in canister sludge is very low. At these low concentrations, the sludge will not exhibit the ignitable properties of relatively pure uranium metal or hydride. It should be noted that fuel wash sludge will contain a significant quantity of fuel (uranium and zircalov) pieces. These will, however, oxidize to a significant extent in the knockout pots prior to being removed from the basins

- The waste matrix cannot sustain vigorous combustion. The definition of ignitable non-liquids includes the requirement that, when ignited, the waste burns so vigorously and persistently that it creates a hazard. The composition of both sludge streams is predominantly water and noncombustible inorganic materials. Even if traces of uranium metal or hydride could ignite, there is insufficient combustible material in the waste to sustain the intensity of combustion described by WAC 173-303-090(5)(a)(ii).
- Samples of sludge and fuel have not ignited during sampling, shipping or handling. Wet sludge samples have been freely handled without special precautions to prevent ignition. A number of these samples have been allowed to dry out, with no evidence of heating or ignition (Baker, Makenas and Pottmeyer, 2000). Small samples of fuel segments (including highly corroded portions of fuel elements, representative of the fuel pieces in fuel wash sludge) have also been handled in the laboratory without special precautions to prevent ignition, and no self-heating or ignition has been observed at standard temperatures. These observations indicate that the sludge streams will not ignite under the conditions required by WAC 173-303-090(5)(a)(ii).
- Test data on sludge and fuel. While the regulations do not specify test methods to determine the ignitability of non-liquids, test methods are available that measure the relative potential for runaway reactions of materials. These methods are useful in predicting the tendency of materials to ignite or react violently. Several such tests have been conducted on sludge and fuel samples, as described below.

Samples of floor and pit sludge and canister sludge have been tested using the Reactive System Screening Tool (RSST). In this test, samples are slowly heated in a reaction vessel and monitored for rapid temperature increases that are indicative of exothermic reactions. Seven samples of floor and pit sludge and one sample of canister sludge were tested by the RSST. None of the samples showed

evidence of reaction through sample dry-out, typically above 200 degrees C (Bechtold, 2000a and Bechtold, 2000b) These data are a strong indication that floor and pit sludge and canister sludge will not ignite under the conditions (standard temperature and pressure) that the regulations specify.

Data supporting the non-ignitability of fuel wash sludge comes from ignition testing and Thermogravimetric Analysis (TGA) on samples of damaged fuel elements from the KW Basin. While these studies were performed to evaluate the safety of the fuel removal and conditioning processes rather than sludge storage, they provide useful information for designation. In ignition testing, both intact and highly corroded fuel segments were heated in air until they ignited. The corroded fuel segments ignited between 277 and 500 degrees C (Abrefah et al., 1999). These ignition temperatures are far higher than the conditions specified by WAC 173-303-090(5)(a)(ii), i.e. standard temperature. The TGA test involves heating small samples of fuel in a controlled atmosphere (moist air, dry air and moist helium) while measuring weight gain in the samples, which is indicative of fuel oxidation. Although some difficulties existed due to sample loss during heating, the results of these tests generally confirm that oxidation rates of even highly corroded fuel are moderate and comparable with expected uranium behavior (Trimble, 1999). Rapid oxidation did not occur until temperatures well above standard temperature were reached. The ignition testing and TGA data demonstrate that even in the absence of water, corroded fuel pieces do not readily ignite under the conditions specified by WAC 173-303-090(5)(a)(ii)

Three factors further mitigate any potential ignitability of fuel wash sludge. First, significant oxidation of fuel pieces will occur as the fuel wash sludge accumulates under water in the knockout pots. Second, the sludge will be maintained in water during transport and storage, which further slows the oxidation rate. Moreover, sludge temperatures will be maintained at temperatures far below the fuel ignition temperatures during removal from the basins, in transport, and during storage at T Plant.

Based on the information summarized above, sufficient knowledge and test data have been developed to conclude that the sludge waste streams do not exhibit the characteristic of ignitability.

## Corrosivity (D002/WSC2)

The sludge waste streams are not corrosive based on pH test data from samples of sludge from the floor and pit of the KE Basin, as well as canister sludge from both basins. The measured pH of water associated with the KE floor and pit sludge ranged from 7.52 to 7.95 (Makenas et al., 1996). The pH of the water associated with the canister sludge from KE ranged from 6.06 to 8.39 (Makenas et al., 1997); canister sludge from KW ranged from 6.3 to 8.0 (Makenas et al., 1998).

While no test data are available for KW floor and pit sludge, the KE sludge is considered to be representative of KW sludge. The KE and KW Basins were operated in a similar manner, including continuous pH adjustment of the basin water, such that similar pH properties would be expected.

### Reactivity (D003)

The sludge streams are not designated as reactive (D003). Based on knowledge of the composition of the sludge and experience in handling sludge, the waste streams do not meet the reactivity criteria that relate to violent reaction of waste under WAC 173-303-090(7)(a)(i), (ii), or (vi) through (viii). As discussed under ignitability above, floor and pit sludge, canister sludge, and highly damaged fuel have been sampled, shipped and handled in the laboratory without evidence of violent reaction or explosion. RSST, TGA and fuel ignition test data further confirm that these waste streams do not react violently or explode under the conditions specified by the regulations.

The sludge does not contain constituents that could release evanides, sulfides, or other toxic gases, vapors or fumes (WAC 173-303-090(7)(a)(iv) and (v)). KE floor and pit sludge samples have been tested for evanide and no evanide has been detected (Makenas et al., 1996).

Regarding WAC 173-303-090(7)(a)(iii), "forms potentially explosive mixtures with water", it has been noted that sludge, particularly canister and fuel wash sludge, evolves hydrogen gas at a steady and predictable rate, both in the basins and under laboratory conditions. The gas generation phenomenon is caused by two factors related to the radioactive component of the waste stream; the oxidation of uranium and uranium hydride in water, and the radiolytic decomposition of hydrogenous material. While the radioactive component of the sludge is not strictly subject to regulation under WAC 173-303, the sludge as a whole has been evaluated against WAC 173-303-090(7)(a)(iii) and determined not to exhibit the characteristic of reactivity. The rationale for this determination is described below.

As with ignitability, the regulations do not specify numerical tests to determine whether a waste forms potentially explosive mixtures with water, leaving some ambiguity in determining whether a waste is reactive by this definition. In promulgating the characteristic of reactivity. EPA clarified the intent of the reactivity characteristic in the preamble to the rulemaking (45 FR 31109):

This definition was intended to identify wastes which, because of their extreme instability and tendency to react violently or explode, pose a problem at all stages of the waste management process.

The preamble text describes a more vigorous and acute type of reaction than the hydrogen generation exhibited by the sludge waste streams. *Extreme instability* is typically associated with compounds such as sodium metal or sodium hydride, which react quickly and vigorously with water such that flammable gas evolution poses an immediate risk of explosion or violent reaction. In contrast, the K Basins sludge waste streams evolve hydrogen gas at a steady and controlled rate, without tendency toward violent or runaway reaction. When mixed with water, the sludge waste streams would continue to evolve hydrogen gas at the same steady, predictable and controlled rate.

The stability of the sludge is due in part to the extent of oxidation of uranium and uranium hydride. Floor, pit sludge and canister sludge have been in continuous contact with water for many years, such that little unoxidized uranium remains, and is distributed throughout the sludge matrix. After initial washing, fuel wash sludge may contain an increased amount of unoxidized uranium. However, this uranium will oxidize extensively under water in the knockout pots prior to removal from the basins. Radiolytic hydrogen gas generation occurs at a steady and predictable rate based on the interaction of radiation emissions and hydrogenous material, and cannot accelerate or become violent

The preamble text also states that reactive wastes are those which, because of their instability, pove a problem at all stages of the waste management process. Experience with the sludge, both in the basins and in the laboratory, indicates that it does not pose such a problem. The sludge has been present in the basins for many years. Simple passive venting of hydrogen gas has been sufficient to mitigate any hazard. Additionally, floor and pit sludge, canister sludge and corroded fuel have been sampled, shipped, and handled in the laboratory with only normal precautions (e.g., venting of containers) used for materials that are known to evolve some hydrogen gas. The normal, passive venting that is required for all transuranic radioactive waste prevents the buildup of potentially explosive concentrations of hydrogen gas. It should be noted that the packaging configuration for the sludge waste streams and the ventilation system in T Plant are more than adequate to prevent buildup of dangerous concentrations of hydrogen gas.

In summary, the sludge waste streams exhibit controlled, steady and predictable evolution of hydrogen gas, which is not subject to the instability or uncontrolled reactions with water that would be characteristic of a reactive waste. As a result, the sludge waste streams do not meet the definition of reactive waste.

#### **Toxicity Characteristic Metals (D004-D011)**

The corrosion products in the sludge streams consist largely of metal oxides, including some of toxicity characteristic metals. ICP analysis (without TCLP extraction) has been performed on many samples of

floor, pit and canister sludge (Makenas et al., 1996; Makenas et al., 1997; Makenas et al., 1998). Cadmium, chromium, lead and silver have been measured in concentrations that could exceed the toxicity characteristic limits, and barium is consistently found in sludge; but the concentrations are below toxicity characteristic levels. Selenium has not been detected by ICP, although detection limits have frequently been above the level required to demonstrate that sludge is below toxicity characteristic levels. Due to difficulty in analysis by ICP, arsenic and mercury have not been reported from ICP analysis.

Additional data regarding arsenic, mercury and selenium are available from analysis of three samples of KE Basin backwash pit sludge by X-Ray Fluorescence (Bechtold, 1994). Arsenic, mercury and selenium were not detected in these samples. Detection limits of the X-Ray Fluorescence method were below the respective toxicity characteristic limits of these metals.

Due to the conditions under which the sludge has formed, it is believed that the primary metals of concern (cadmium, chromium, lead and silver), as well as other metals, would be relatively insoluble under TCLP conditions. To determine whether the sludge would designate for toxicity characteristic metals, the Spent Nuclear Fuel Project, with Ecology and EPA involvement and concurrence, developed data quality objectives (Makenas, 2000) and a sampling and analysis plan (Baker, Welsh and Makenas, 2000) to test composites of existing samples of KE sludge using the TCLP extraction. In accordance with the sampling and analysis plan, two composite samples were developed to be representative of KE Basin floor and pit sludge, white a third composite was representative of canister sludge. The sludge samples were analyzed for arsenic, barium, cadmium, chromium, lead, selenium and silver. The DQO participants, including Ecology and EPA, concurred that mercury is not a constituent of concern (Makenas, 2000 and Bartz and Gadbois, 2000). Analysis of the sludge composite samples was performed on TCLP extracts and for total metals, which could allow some comparison with existing total metals data in KW Basin sludge.

The analysis data show that KE Basin sludge does not designate for toxicity characteristic metals (Loscoe, 2000). Table 2 provides a summary of these data. For simplicity, the table presents the average of the analysis result and any duplicate and replicate analyses performed. Variation among duplicate and replicate analyses was low and other quality control parameters indicate that data are usable for designation. Ecology and EPA have provided their concurrence with this designation for toxicity characteristic metals (Bartz and Gadbois, 2000).

Table 2 - Summary of TCLP Test Data

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	;	Concentration (mg/L) - Average of result, duplicate and replicate analyses			
Metal	Regulatory				
victat	Limit (mg/L)	KE Floor and Pit	KE Floor Sludge	KE Canister Sludge	
	:	Sludge (222-S)	(325 Laboratory)	(325 Laboratory)	
Arsenic	5,0	. 10	0.25	0.25	
Barium	100.0	1.82	6.84	2.36	
Cadmium	1.0	0.653	0.64	0.18	
Chromium	. 5.0	0.222	1.17	0.33	
Lead	5.0	1 (!	0.87	1,33	
Selenium	1.0	. ) ()	().33	0.43	
Silver	5.0	0.144	0.26	0.50	

Since the KE and KW basins managed the same types of fittel and were operated in a similar manner. KW Basin sludge is expected to have the same designation. To confirm this expectation, both TCLP extracts and total metals digestions were performed on KE composite samples. These data could be used to form a ratio of the TCLP result to its corresponding total metal, which could be multiplied by KW sludge results to estimate the possible TCLP concentration of KW sludge. One limitation of this approach is that a meaningful ratio of TCLP to total metal can only be determined if the total metal result is above its detection limit

Using this approach. Table 3 provides estimated KW canister sludge TCLP concentrations for some toxicity characteristic metals. Within the limitations of the available data, this serves to confirm that KW canister sludge should not designate for toxicity characteristic metals.

Table 3 - Estimation of KW Sludge TCLP Concentration

Metal	Ratio of KE	KW Camster Sludge	Estimated KW	Regulatory			
	TCLP/Total	Total metals (mg/kg)	TCLP (mg/l)	Limit			
KE Cani	KE Canister Sludge Composite						
Ba	0.03491	121 59	4.25	100			
Cr	0,00667	184,25	1.23				
KE Floo	r/Pit Sludge Cor	nposite (222-S)					
Ba	0.02117	121.59	2.57	100			
Cd	0.02098	45,36	0.95	, 1			
Cr	0.00069	184.25	0.13	5			
Pb	< 0.00342	453,81	1:55	5			
KE Floo	KE Floor Sludge Composite (325)						
Ba	0.12220	121.59	14.86	. 100			
Cd	0.01384	45.36	0.63	1			
Cr	0,00600	184 25	1 11	5			
Pb	0.00854	453.81	3,87	.5			

This value is the average total metal concentration in 8 samples of as-settled sludge (provided in Makenas et al., 1998, Appendix B). When one or more results were below detection levels, 0.5 times the reported limit of detection was used to form the average

A number of limitations exist to the approach provided in Table 3. No estimates could be obtained for arsenic because the KW canister sludge analyses did not provide arsenic results. Additionally, no estimates could be established for selenium or silver because these metals were below the limit of detection in all of the KE sludge total metals analyses. Further, the KW canister sludge data had severely elevated detection limits for some metals, particularly cadmium, lead, selenium and silver. In some cases, many or all of the KW canister sludge samples were less than these elevated detection limits for metals, which results in biased mean of the metals concentration. One approach to offsetting this bias is to set results below detection limits to a value equal to one half the detection limit (Gilbert, 1987). This approach was used to establish the mean concentration of the total metal concentration in KW canister sludge used in Table 3.

Despite these limitations, the data provide general confirmation that KW sludge designates the same as KE sludge. Of the toxicity characteristic metals, chromium and lead are consistently found in sludge in the highest concentrations. The estimated KW TCLP concentrations confirm that KW sludge would not fail TCLP for chromium and lead. Similarly, cadmium and barium calculate out to an estimated TCLP concentration below the regulatory limit. When combined with the process knowledge that KE and KW operations were similar, this provides reasonable assurance that KW sludge would pass TCLP testing just as the KE sludge composites did

#### **Toxicity Characteristic Organics (D012-D043)**

The two sludge waste streams do not designate for the toxicity characteristic pesticides, herbicides of other organies based on knowledge of the fuel manufacturing process and fuel storage processes in the KE and KW Basins and test data. As manufactured for use in Hanford's N-Reactor, the fuel was highly purified uranium metal with a zircaloy cladding; no organic compounds could be present in the fuel None of the specific D012 - D043 toxicity characteristic constituents are known to have been used in applied to, or discharged to the basins

As confirmation of this knowledge, analysis of five sludge samples from the KE Basin and two samples from the KE Weasel Pit for volatile and semivolatile organic compounds identified none in concentrations approaching the toxicity characteristic limits (Makenas et al., 1996). It should be noted that there were

some quality control problems with these samples, particularly low-level contamination of blanks and poor surrogate recoveries for semi-volatile organics. Nevertheless, use of these data as semi-quantitative data provides reasonable confirmation that the sludge does not designate for toxicity characteristic organic constituents.

While participating in the development of the data quality objectives and sampling and analysis plan for TCLP testing of the sludge (see previous section). Ecology and EPA concurred that toxicity characteristic organic compounds are not constituents of concern in the KE and KW sludge waste streams (Bartz and Gadbois, 2000)

## Criteria Designation

#### Toxicity

The sludge waste streams do not designate as toxic dangerous waste based on ICP, anion analysis: X-ray diffraction and process knowledge that have been used to identify the overall chemical composition of the KE and KW sludge. This composition is described in 105-K Basin Meterial Design Basis Feed. Description for Spent Nuclear Fiel Project Facilities, Volume 2. (Pearce, 2000). The majority of the sludge is in the form of insoluble solids (e.g., sand) and the oxides and hydroxides of aluminum, iron, zirconium, and uranium, as well as other metals in trace concentrations. Using the book designation methodology of WAC 173-303-100(5)(b) and these composition data, neither sludge stream is a dangerous waste by the toxicity criteria.

Only five of the discrete chemical constituents identified in 105-K Basin Material Design Basis Feed Description for Spent Nuclear Finel Project Facilities. Volume 2 are Toxic Category D or more toxic based on data from the Registry of Toxic Effects of Chemical Substances. The major constituents in the sludge waste streams, including uranium metal, uranium hydride, and oxides of aluminum, calcium, iron, magnesium, silicon, sodium and uranium, are either less toxic than Toxic Category D or have no relevant toxicity data in the Registry of Toxic Effects of Chemical Substances.

Table 4 presents the equivalent concentration calculation for the five constituents that are toxic in accordance with WAC 173-303-100(5)(b). The columns titled "Max Weight Percent" list the highest concentration of each constituent in the various substreams from the appendices of 105-K Basin Material Design Basis Feed Description for Spent Nuclear Fuel Project Facilities. Volume 2. (It should be noted that considerable conservatism exists by use of the highest values from each substream and by using dry weight percents of sludge.) The columns titled "Equivalent Concentration" list the calculated equivalent concentration of toxic constituents as specified by WAC 173-303-100(5)(b). The total equivalent concentrations of 0.00054% for floor and pit sludge and 0.00007% for canister and fuel wash sludge are below the threshold equivalent concentration of 0.001% to be regulated as a toxic dangerous waste

Table 4 - Washington Toxicity Book Designation

	i abie 4	- wasnington	loxicity Book	Designation	•
	Toxic	Floor and Pit Sludge		Canister and Fuel Wash Sludge	
Constituent/CAS#		Max Weight	Equivalent	Max. Weight	Equivalent
·	Category	Percent	Concentration	Percent	Concentration
Silver oxide 20667-12-3	D	0:0021	0,00000021	0.011	0 0000011
Bismuth oxide 1304-76-3	. D	0	(1)	0.047	0.0000047
Cadmium oxide 1306-19-0	C	0.019	0.00019	0,0096	0 0000096
Cuprous oxide 1317-39-1	<u>(</u> ,	. () (19]	0 000091	0.055	0,000055
Thallium oxide 1314-32-5	- 13	0.043	0,00043	()	0
Total Equivalent Concentration			0.00054		0,00007

#### Persistence

Based on knowledge of the KE and KW Basin operations and test data, the sludge waste streams do not designate as persistent waste. Except for a brief period in 1980 and 1981 during which algicides were applied to the basin water, halogenated organic compounds were not used in or discharged to the basins. Semivolatile organic analysis of sludge samples identified no halogenated organic compounds other than the PCBs previously discussed in the section on Regulation under Other Laws (Makenas et al., 1996; Makenas et al., 1997, Makenas et al., 1998). While already regulated under TSCA, the concentration of PCBs were evaluated against the persistence criterion as well, and found to be below the regulatory threshold of 0.01% by weight based on the test data described below.

Seven samples of floor and pit sludge were tested for PCBs as described in Makenas et al., 1999. The PCB concentration of the floor and pit sludge samples are provided in Table 5, using the adjusted concentration of PCBs (Makenas et al., 1999, Appendix B) in settled sludge and averaging duplicate/replicate analyses of the same sample. The mean concentration of these samples is 46 ppm, or 0.0046% by weight.

Table 5 - Summary of PCB Test Data for Persistence Designation

Sample Number	Sampling Location		Concentration in Settled Sludge (ug/g)	
KES-I-15	KE Basin floor		63	
KES-L-1	KE Basın floor		17 (not detected)	
KES-A-2	KE Basın floor		· 14 (not detected)	
KES-N-5	KE Basın floor	1	79 (not detected)	
KES-H-8	KE Basin floor		- 16 (not detected)	
KES-P-16	Weasel pit		36	
KES-R-18	Weasel pit	17 1 MA 3001 MINO 107 1 A4 11 MAN AN ANALAS ANA	94	
	Mea	nn concentration	46	

I Nondetected results were used at the method quantitation limit

PCB concentrations in canister sludge were much lower than in the floor and pit sludge. Nine samples of KE canister sludge were analyzed, ranging from nondetectable to a maximum of 1.1 ug/g (Makenas et al., 1997). Seven samples of KW canister sludge were analyzed, ranging from nondetectable to a maximum of 5.73 ug/g

The sludge streams do not designate as WP03 for polycyclic aromatic hydrocarbons (PAHs) based on test data. A number of sludge samples have been tested for Total Organic Carbon (TOC) and the TOC concentrations are far below the 1% PAH threshold for regulation as a WP03 waste (Makenas et al., 1996; Makenas et al., 1997; Makenas et al., 1998)

## Conclusion

Test data from samples of KE and KW sludge waste streams, combined with knowledge of the waste generating process and the composition and properties of the sludge, show that the sludge waste streams will not designate as a dangerous waste under WAC 173-303.

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September 14, 2000

Phillip G. Loscoe, Director Office of Spent Nuclear Fuels U.S. Department of Energy P.O. Box 550, MSIN: S7-41 Richland, Washington 99352

Dear Mr. Loscoe:

Re: Response to "Transmittal of Final Laboratory Data Reports for Toxicity Characteristic Leaching Procedure (TCLP) Analyses Performed on K-East (KE) Basin Sludge Samples," letter from P.G. Loscoe to Joan K. Bartz and Larry E. Gadbois, dated August 8, 2000

The Washington State Department of Ecology (Ecology) and the U.S. Environmental Protection Agency (EPA) have reviewed the subject data reports prepared by the 222-S Laboratory (Fluor Hanford, Inc.) and by the 327/325 Laboratories (Pacific Northwest National Laboratory) for the U.S. Department of Energy (USDOE). Ecology and EPA concur that the data are acceptable for use and that the data demonstrate that the K-East Basin sludges do not designate as Toxic for metals.

Ecology, EPA, and USDOE and its contractors have worked together since November 1999 to ensure that the sampling and analysis of these sludges would be acceptable and the approach to data interpretation would be understood by all parties. The following reiterates the agreements made during our meetings. (The quotes are from the subject letter with some further information which we believe is important to document.)

- (1) "The method in which sludge samples had been collected from the basin, including composites, was sufficient to ensure representative samples were available for analyses."
- "The sample size for TCLP, although smaller than typically analyzed in a non-radioactive environment, was sufficient given the methodology for running duplicates and splits." Ecology requested a target test portion of 10 grams minimum and replicate extractions so that the precision of the extraction and nature of the sample material could be evaluated. Ecology also requested analysis of total metals for comparison to the data from the extraction so that the consistency and reasonableness of the data could be established. See item (4) for further use of the total metals data.
- (3) "TCLP analysis for organic constituents was not necessary, based on process knowledge of the waste. Only the heavy metals of concern would be analyzed." Although polychlorinated biphenyls are known constituents of the sludges, Ecology agreed to eliminate analysis of the organics on the Toxicity Characteristic list. In addition, Ecology agreed to omit mercury from the determination.

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- (4) "Both the KE and K-West (KW) Basins contain SNF (Spent Nuclear Fuel) from N
  Basins. The accumulated sludge in the KE and KW Basins would be considered sufficiently similar that TCLP data from the KE Basin (sludge) could be used to calculate the TCLP concentration in the KW Basin (sludge) by direct comparison to the total metals data in each basin. This would eliminate the need to run separate TCLP analyses of the sludge from the KW Basin." (Italicized words in parentheses are added for clarity.) Ecology agrees that this is a reasonable basis for making a waste designation for the K-West Basin sludges, based upon process knowledge.
- (5) "Holding times for the KE Basin samples could exceed the standard times for TCLP analysis, since only metals were being analyzed and metals would not be affected by longer holding times." Ecology had no concerns about biological activity or chemical volatility affecting the samples. Ecology did ask that the holding times for the prepared extractions and digestates be enforced.
- (6) The revised Data Quality Objectives document and the Sampling and Analysis Plan were provided to Ecology and EPA for review and comment. All issues were satisfactorily addressed before the analytical work was performed.

Ecology and EPA evaluated the results of the analyses to ensure that the numerical results support the conclusion that the results for TCLP extractable metals are below the threshold for regulation as dangerous waste. The referenced transmittal letter states that "heavy metal concentrations are far below the threshold for regulation as dangerous waste..." This is generally true, with the exception of cadmium results from the 222-S Laboratory which were 65 percent of the Toxicity Characteristic limit, and selenium results from the Pacific Northwest National Laboratory which were as high as 50 percent of the Toxicity Characteristic limit. The quality control data for these analyses were notably good, thus supporting the conclusion that cadmium and selenium are below the threshold for regulation. The final results for all other analytes support the conclusion that Toxic metal concentrations are far below the threshold for regulation.

Ecology and EPA note that an error was made in the test portion to extraction solution ratio in the 222-S Laboratory (1:14 was used instead of 1:20), but agree that the resulting data still may be used for waste designation of these sludges.

Ecology and EPA also reviewed the supporting quality control data. A number of quality control deficiencies were noted. The more significant deficiencies are listed below:

- Spike recoveries for silver and selenium and barium recovery in the soil standard at the 222-S Laboratory were slightly outside target results. However, the sample results for these three analytes were well below the Toxicity Characteristic limits.
- The chromium in the soil standard at the 222-S Laboratory deviated substantially from the prediction interval; however, sludge sample results for chromium were very low relative to the Toxicity Characteristic limits.

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- Matrix spike recoveries for silver in several of the 327/325 Laboratory quality control samples were outside target ranges. However, silver results in sludge samples were very low relative to Toxicity Characteristic limits. In addition, this situation is commonly observed for the TCLP extraction/digestion procedures and is an inherent problem in the procedure.
- Relative percent differences between a sample and its duplicate for silver, barium, cadmium, chromium, and lead exceeded "acceptance" limits of 20 percent. These analytes all had low concentrations in sludge samples relative to the Toxicity Characteristic limits. More importantly, these data are related to the nature of the sample material and do not relate to the acceptability of the analytical data for use in waste designation.

Although these quality control issues introduce additional uncertainty in some of the results, the analytes with increased uncertainty are those with low concentration relative to the Toxicity Characteristic limits. Therefore, Ecology and EPA agree that these data support the conclusion that, based on Toxic metal concentrations, the sludges are below the threshold for regulation as dangerous waste.

If you have any questions regarding this letter, please contact Greta Davis, T Plant Permit Writer for Ecology, at 376-3025 or Larry Gadbois with EPA at 376-9884.

Sincerely,

Joan K. Bartz

Nuclear Waste Program Chemist

Department of Ecology

Sincerely,

Larry Gadbois,

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